Amide group formation during oxidation of poly(oxyalkylene) derivatives of ethylenediamine*

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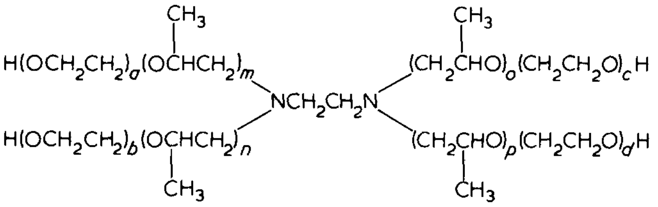
It was shown that in the process of thermooxidative decomposition of the poly(oxyalkylene) derivatives of ethyoenediamine the amine groups undergo a partial transformation to formamide groups. In the case of decomposition of the model substance, *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine, the *N,N*-di(2-hydroxypropyl) formamide was formed.

INTRODUCTION

During our studies on oxidation and thermooxidation of block copolymers of ethylene oxide (EO) and propylene oxide (PO) based on ethylenediamine as an initiator (so called tetronic-type copolymers[1])



it was found[2] that the i.r. spectrum of the oxidized product, along with a band characteristic for the carbonyl group (ester) having a maximum at 1725–1730 cm^{-1}, contains a band at 1675 cm^{-1}. This latter band was found to be absent in the spectra of oxidation products derived from alkylene oxide copolymers containing no amine groups in the molecule. On the basis of results reported by Noskov on thermooxidative[3] and photooxidative[4] decomposition of some epoxide oligomers cured with phenylenediamine, it seems possible that the band in question may be caused by the presence of the amide groups.

The purpose of the present work was to clarify this problem.

EXPERIMENTAL

N,N,N',N',-tetra (2-hydroxypropyl) ethylenediamine was obtained by the autocatalytic addition of 4 moles of PO to 1 mole of ethylenediamine at 373 K.

The tetronic-type copolymers were prepared by the successive addition of PO and EO to *N,N,N',N'*-tetra (2-hydroxypropyl) ethylenediamine at 373 K in the presence of 0.25% NaOH as a catalyst. The characteristics of the products are given in *Table 1*

N,N-di(2-hydroxypropyl) formamide was obtained from diisopropanolamine via acylation with ethyl formate.

Thermooxidative decomposition of the copolymers studied as well as that of *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine was carried out in bulk at 393 K under the oxygen atmosphere exactly as reported earlier[5].

The course of the decomposition was followed by the i.r. and ^{1}H-n.m.r. methods. The measurements of i.r. spectra were carried out with a Perkin–Elmer model 621 spectrophotometer using liquid films ~0.01 mm thick, in the region from 200 to 4000 cm^{-1}. ^{1}H-n.m.r. spectra were recorded with a Tesla BS-487 80 MHz instrument using HMDS as an internal standard, for 8–15 wt% solutions of studied compounds in CCl_4 (in the case of *N,N*-di (2-hydroxypropyl) formamide TMS as an internal standard and $CDCl_3$ as a solvent were used); the temperature of the measurement was the ambient one or 323 K.

For some of the decomposition products quantitative nitrogen determinations were carried out according to Lassaigne.

The separation of EO and PO adducts to ethylenediamine from neutral products was carried out by sorption of ionic species from a methanol solution on a macroporous cation exchanger Amberlyst 15, Rohm and

Table 1 Characteristics of copolymers studied

Sample symbol[a]	$\bar{M}_n$ of copolymer[b]	EO content[c] wt %	Nitrogen content[c] wt %	Neutral products content wt %
1000/40	1560	37.5	1.68	9.9
1800/40	2780	37.2	0.60	19.3
2000/40	3560	44.7	0.34	29.7

[a] The first number refers to the approximate $\bar{M}_n$ value of the hydrophobic group, the second—the approximate weight fraction of ethylene oxide in the copolymer molecule
[b] The number-average molecular weight of the copolymer was determined by the vapour osmometry
[c] Calculated from the synthesis

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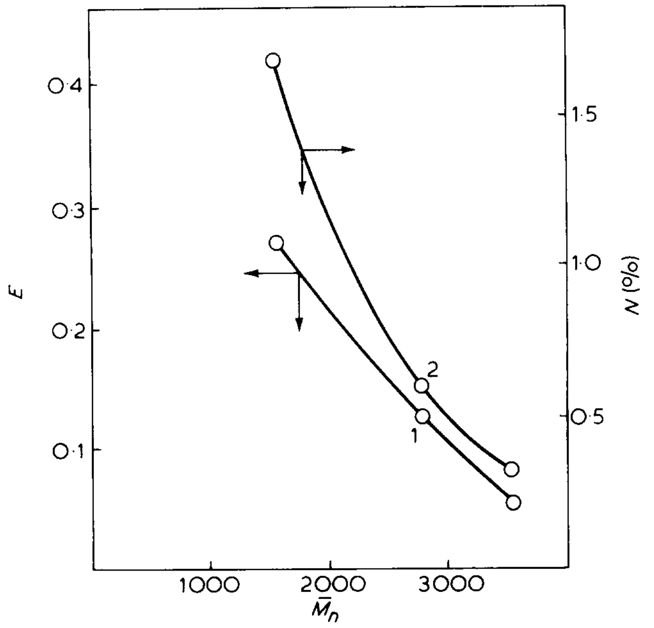


Figure 1 Relationship between values of extinction at 1675 cm^{-1} (curve 1) for oxidized (T = 393 K) copolymers of tetronic type and nitrogen content (curve 2) in starting copolymers vs. their $\bar{M}_n$. The degree of decomposition corresponds to evolution of 5 g of volatile products per 100 g of initial sample

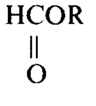
Haas Co., USA. The basic product desorption was performed using a 10% dimethylamine solution in methanol.

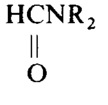
RESULTS AND DISCUSSION

In the case of thermooxidative decomposition of the tetronic type copolymers with constant EO content in the macromolecule, yet having varying $\bar{M}_n$ values, we found that there is a distinct relationship between oxidized polymer extinction values at 1675 cm^{-1} and amine nitrogen content in the macromolecule (*Figure 1*).

It can be seen in *Figure 2* that the appearance of the absorption band with a maximum at 1675 cm^{-1} is associated with the neutral fraction of the oxidized product in which the presence of chemically bound nitrogen has been established. This fraction was separated from the basic copolymer containing amine groups by using a macroporous cation exchanger.

In the ^{1}H-n.m.r. spectrum of the neutral fraction at high gain, among others, two signals of 8.25 and 8.35 were observed (*Figure 3a*). These signals may be assigned to the formyl protons in esters and amides of formic acid. According to literature data, the values of chemical shifts for these protons are as follows:


$\underset{\underset{\displaystyle O}{\|}}{HCOR}$ 8.0–8.2 ppm [6]


$\underset{\underset{\displaystyle O}{\|}}{HCNR_2}$ 7.9–8.1 ppm [6]

Small differences between values obtained in this work and literature data might have arisen from using different standards (HMDS in place of TMS). The ester origin of a signal at 8.35 ppm seems to be established by its disappearance following hydrolysis of the neutral fraction (*Figure 3b*). A similar process has also been observed in the i.r. spectrum (*Figures 4a* and *4b*), since, following hydrolysis, only the band having a maximum at 1675 cm^{-1} could be observed.

The facts presented above confirm that as a result of thermooxidation of the tetronic-type copolymers some of the amine groups underwent transformation into amide groups. In view of considerable difficulties in the isolation of the amide formed from a mixture of poly(oxyalkylene glycols) contained in the neutral fraction, in order to determine the probable structure of this compound further attempts were made to isolate an analogous

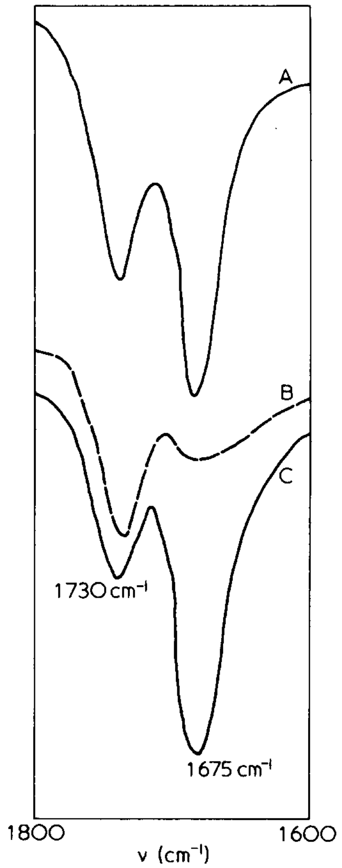


Figure 2 I.r. spectra of oxidation products derived from the 1000/40 tetronic-type copolymers (temperature of oxidation = 393K, reaction time = 6 h); (a) oxidized copolymer, (b) copolymer fraction free of neutral products, (c) neutral fraction

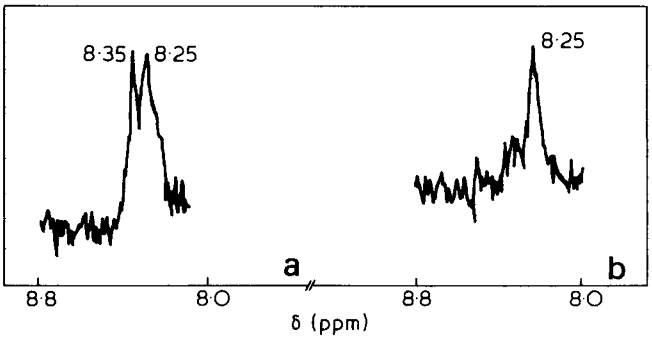


Figure 3 ^{1}H–N.m.r. spectrum of the neutral fraction derived from the oxidized 1000/40 tetronic-type copolymer: (a) before, and (b) after hydrolysis. T = 393 K, oxidation time = 32 h

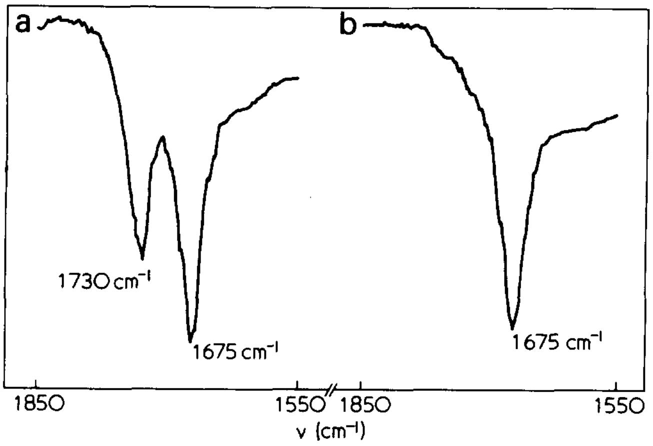


Figure 4 I.r. spectra of the neutral fraction derived from the oxidized 1000/40 tetronic-type copolymer: (a) before, and (b) after hydrolysis. T = 393 K, oxidation time = 32 h

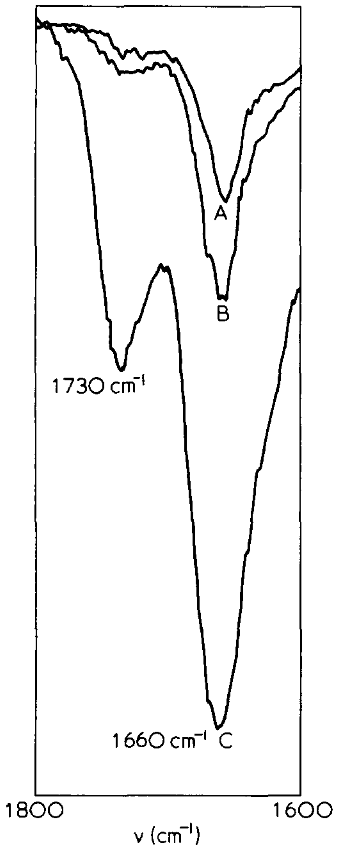


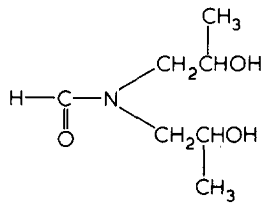
Figure 5 I.r. spectra of *N,N,N',N'*-tetra (2-hydroxypropyl)ethylenediamine oxidized at 393 K for (a) 7 h, (b) 13 h, and (c) 22 h

decomposition product from the oxidized *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine. This compound forms the centre of the tetronic-type copolymer.

In the i.r. spectrum of the oxidized *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine (*Figure 5*), along a band with a maximum at 1730 cm^{-1}, another band having a maximum at 1660 cm^{-1} appeared. This band was found to be slightly shifted as compared to that in the oxidized copolymer which may be caused by the absence of oxyalkylene groups in the molecule. The intensity of both these bands was found to increase with increasing degree of oxidation, but the 1660–1730 cm^{-1} band intensity ratio was considerably greater than that found in the case of the copolymers. This may be associated with a higher amine nitrogen content in *N,N,N',N'*-tetra(2-hydroxypropyl) ethylenediamine, equal to 10.4 wt %.

As in the case of the copolymer, the neutral fraction was separated from the oxidized *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine with the aid of an ion exchanger. The yield of this fraction after decomposition times of 7 and 22 h was 3.8 and 5.8 wt %, respectively. On standing, this fraction separated into two immiscible layers: a colourless and a yellow one, where the former exhibited a characteristic absorption band at 1730 cm^{-1}, and the latter, at 1660 cm^{-1}. The yellow fraction yield decreased with increasing degree of decomposition of *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine. This product was purified by extraction with CCl_4 (it was only slightly soluble in this solvent). No absorption at 1730 cm^{-1} could be detected after such purification. The isolated compound was then characterized by the ^1H–n.m.r. technique – its spectrum is shown in *Figure 6* and its interpretation in *Table 2*.

The obtained results allowed us to assign the structure of *N,N*-di(2-hydroxypropyl)formamide to this compound:



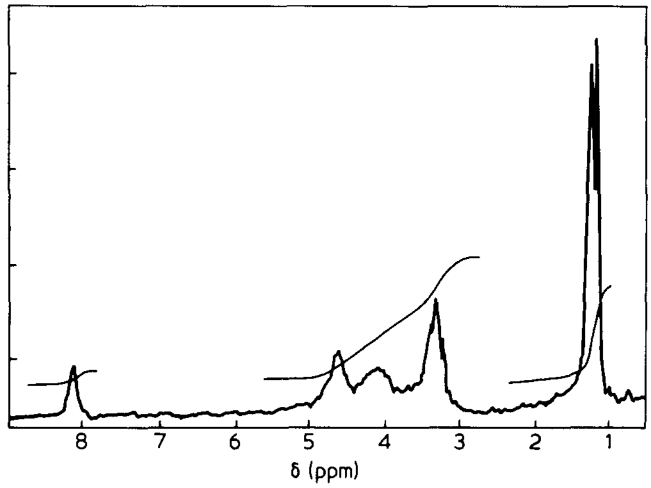


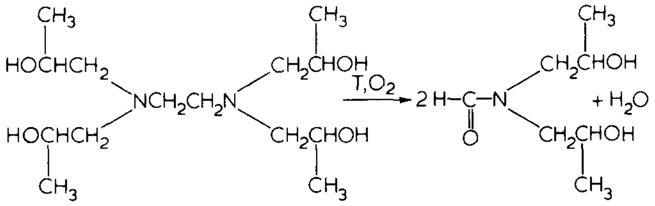
Figure 6 ^1H–N.m.r. spectrum of *N,N*-di(2-hydroxypropyl)formamide prepared via oxidative decomposition of *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine

Table 2 ^1H–N.m.r. data for the compound separated from the oxidized *N,N,N',N'*-tetra(2-hydroxypropyl)ethylenediamine (standard: TMS; solvent; $CDCl_3$; temperature: ambient and 323 K^x)

Chemical shift value (ppm)	Protons in the group	Number of protons calculated from integration results
1.2–1.3 (doublet)	$-CH_3$	6
3.2–3.4	$-CH_2-$	4
3.9–4.2	$-CH$	2
4.5–4.8	$-OH$	2
4.0–4.3^x		
8.1–8.2	$\underset{\underset{O}{\Vert}}{N-CH}$	1

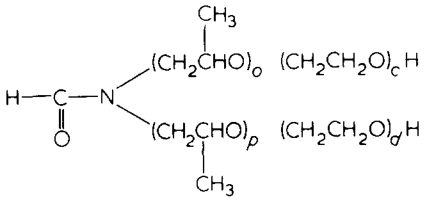
The above structure was confirmed by the i.r. analysis. The following absorption bands were assigned: $-CO-N$ (1600 cm^{-1}), $C-N$ (1220, 1190, 1130 cm^{-1}), $CH-OH$ (3500–3200, 1400, 1340, 1130, 1080 cm^{-1}), $-CH_2-$, $-CH_3$ (2980–2880, 1400, 1440, 1375 cm^{-1}).

To confirm the proposed assignment, the compound in question was synthesized and analysed by i.r. and ^1H-n.m.r. The obtained spectra of the synthesized *N,N*-di(2-hydroxypropyl)formamide were found to agree well with those for the identified product of decomposition which proves its structure. The probable reaction scheme leading to *N,N*-di(2-hydroxypropyl)formamide formation may be:

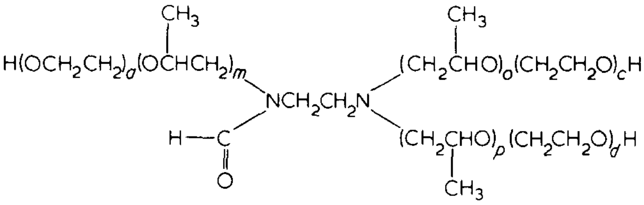


It has been reported[7] that water is the major constituent of the volatile products being formed during thermooxidative decomposition of *N,N,N′,N′*-tetra(2-hydroxypropyl)ethylenediamine (~93 vol% after decomposition time of 22 h).

The results indicate that during thermooxidative decomposition of polyoxyalkylene derivatives of ethylenediamine of the tetronic-type some of their amine groups undergo transformation into formamide ones. The formamide group formation proceeding through cleavage of the C–C bond in the centre of the molecule



does not exclude the possibility of its formation via scission of at least one polyoxyalkylene chain from the copolymer molecule



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